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Carbon and nitrogen stable isotope measurements of bulk organic matter in sediments from Obanul Mare paleolake, Mangalia, Romania

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Pleistocene climate changes have led to vegetation type and distribution changes. In Central-Eastern Europe, long paleoenvironmental archives are scarce, thus for this region environmental reconstructions on glacial/interglacial time scales are not available.

In eastern Romania, near the Black Sea, a series of deep collapse dolines functioned as lakes and accumulated thick sedimentary sequences (Constantinescu & Constantin, 2001) that could have deposited during the Pleistocene. Recently, a 60 meters long core was retrieved from the Obanul Mare paleolake in order to study biogeochemical environmental proxies throughout the existence of the lake. In this study, we present preliminary $\delta^{13}C$ and $\delta^{15}N$ measurements of bulk organic matter and bulk carbon content of these sediments.

The samples were chosen along the entire length of the sediment core in order to investigate if there are significant changes regarding the $\delta^{13}C$. The sections of the sedimentary sequence are well defined, starting with the recent soil and brown clays and continuing with yellowish and yellowish-reddish deposits, a segment with dark gray clays, to the last unit of the core characterized by gravels and limestone blocks.

The samples were analyzed for total carbon isotopes ($\delta^{13}C_{total}$), organic carbon isotopes ($\delta^{13}C_{org}$), total nitrogen isotopes ($\delta^{15}N$), and C/N. For the measurement of $\delta^{13}C$, bulk sediment samples from various depths were collected and processed using a decalcification method by wet chemical treatment, slightly modified after Pötter *et al.* (2021). Before acid treatment, 5 g of each sample were dried in a drying oven at 60 °C for 24 h and in order to obtain a homogenized sample, they were ground thoroughly in a mortar with pestle. Approximately 150 mg were weighed from each sample in centrifuge tubes, treated with 25 mL of 1 M hydrochloric acid (HCl) which corresponds to a concentration of 5% HCl and kept in water bath for 4 hours at a 50 °C. After digestion, the sediment samples were sequentially rinsed twice with 40 mL of ultrapure water and centrifuged between rinses, in order to remove any remaining HCl. The final preparation step consists in drying the samples in a drying-oven at 60 °C overnight.

Samples were analyzed at the Stable Isotopes Laboratory of the Research Institute of the University of Bucharest (ICUB-SIL) using a Nu Instruments Horizon 2 IRMS coupled to a EuroVector 3024 elemental analyzer.

Calibrations were performed using three organic reference standards: two internal standards, Blue Grama, a C4 plant, and a C3 soil standard, whose standard deviation within-sequence was 0.09‰, 0.09‰ for $\delta^{13}C$ and 0.85‰, 0.4‰ for $\delta^{15}N$, respectively. We also used international standards, IAEA-CH3, a pure substance with known values and with a standard deviation of 0.09‰ for $\delta^{13}C$.

The organic carbon content is highest in the present-day soil (~2%) but decreases sharply to 0.2% in the underlying sediments. The N content of the topsoil is 0.2% and decreases to an average of

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0.03%, with a resulting organic C/N ratio varying between 7 and 11. The sedimentary organic matter origin can be evaluated due to the C/N ratio and for C/N values lower than 10, we can assert that the organic material can be derived from lacustrine phytoplankton compared with terrestrial organic components that point to a ratio higher than 20 (Leng *et al.*, 2005).

$\delta^{15}N_{total}$ values vary between 6‰ and 10‰ (vs AIR), while $\delta^{13}C_{org}$ is relatively stable throughout the dataset, varying very little around an average of -25.5‰ (vs VPDB), thus showing that the main contributor to sediment organic carbon was C3 terrestrial plants.

The existence of a sulphidic aquifer extending in the region around Obanul Mare promoted the presence of a chemoautotrophic ecosystem, whose isotopic signature is different from its surroundings (Sârbu *et al.*, 1996). Its $\delta^{15}N$ values vary between ~-10‰ and ~0‰, while $\delta^{13}C$ values do not surpass -30‰. Thus, we can state that from our preliminary measurements we do not discern the sulphidic ecosystem as a source of organic content into the lake.

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